Lawrence Livermore National Laboratory

Denitrification and nitrate transport in groundwater underlying dairy operations in California's Central Valley

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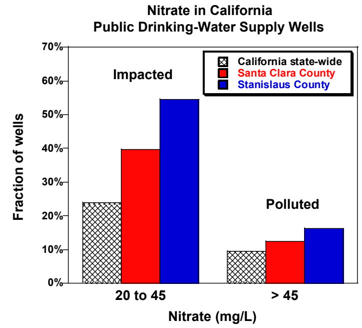
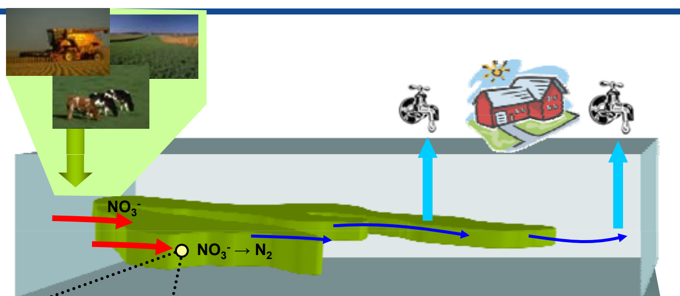
Nitrate is also the #1 drinking-water contaminant in California groundwater:



- **California has lost one-third of its public drinking-water wells since 1988!**
  - Nitrate is most contaminant cited for abandonment
  - Dairy groundwaters
- **Groundwater supply about half of California's public water supply**

Saturated-zone denitrification may mitigate the impact of nitrate contamination on drinking water wells under the right conditions

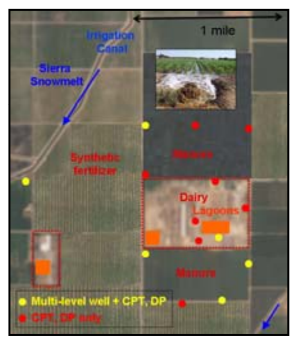


DENITRIFICATION: Microbial conversion of nitrate to molecular nitrogen

Does saturated-zone denitrification provide a sink for some agricultural nitrate?

Is nitrate from agriculture transported conservatively?

We instrumented a dairy in California's Central Valley to develop new methods for investigating denitrification



A dairy in Kings County, California

Distal Kings River alluvial fan deposits, intergrading with Tulare Lake sediments

- **CPT and Direct Push Sampling**
  - Hydrostratigraphy/lithology
  - Nitrate, excess N_2, and sediment samples
  - Redox conditions
- **Multiple-depth monitoring wells**
  - Water levels and chemistry
  - Excess "nitrogen"
  - Water and nitrate isotopic composition
  - Tritium/helium-3 groundwater age dates, recharge temperature & excess air

The end product of denitrification is molecular nitrogen

$NO_3^- \rightarrow$	$NO_2^- \rightarrow$	$NO \rightarrow$	$N_20 \rightarrow$	N_2
Nitrate	Nitrite	Nitric Oxide	Nitrous Oxide	Nitrogen

Denitrification requires
- Denitrifying bacteria
- Low oxygen conditions (< 0.6 mg/L)
- An electron donor (organic carbon; pyrite)

Methods for detecting denitrification
- Groundwater chemistry (loss of nitrate along a flowpath under low-oxygen conditions)
- **Build-up of end-product nitrogen**
- Presence of denitrifying bacterial populations
- Changes in isotopic composition of nitrate and of electron donors

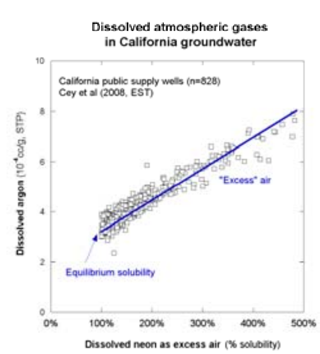
Groundwater contains atmospheric nitrogen above equilibrium solubility

Denitrification: $NO_3^- \rightarrow N_2$

Point 1: Groundwater contains atmospheric gas (including nitrogen)
The presence of dissolved nitrogen in groundwater does not by itself indicate denitrification

Point 2: Groundwater contains more atmospheric gas (including nitrogen) than predicted by equilibrium solubility
The atmospheric gas component must be measured for each sample.

Point : High levels of excess air in artificially recharged groundwater will also have high levels of oxygen
Style of recharge may affect nitrate transport and degradation



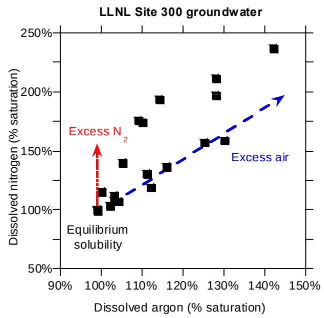
Excess nitrogen in groundwater
"Excess" N_2 is the non-atmospheric N_2 component

Excess N_2 = Total N_2 – Atmospheric N_2

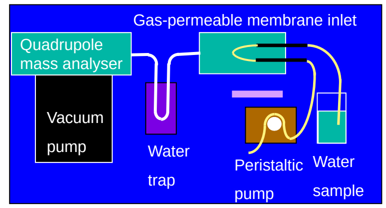
Excess nitrogen is determined by measuring an inert atmospheric gas such as argon.

- Measure total dissolved nitrogen
- Measuring an inert atmospheric gas(Ar, Ne)
- Estimate atmospheric N_2 with an excess air model or an observed trend in non-denitrified groundwater
- Subtract the atmospheric nitrogen component

Assume that excess nitrogen is derived from denitrification



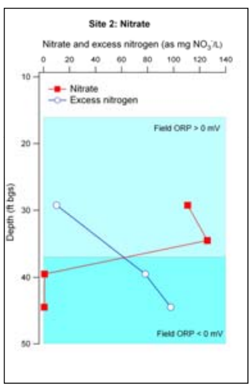
Determination of excess nitrogen using a simple gas analyzer



Membrane inlet mass spectrometry (MIMS)

- Measures nitrogen, argon, oxygen, carbon dioxide, and methane
- Fast, field-portable, and inexpensive
- Uses standard VOC sampling method: three 40-mL VOA vials with no headspace

Field determination of excess nitrogen in a redox-stratified aquifer



Excess nitrogen was determined in the field

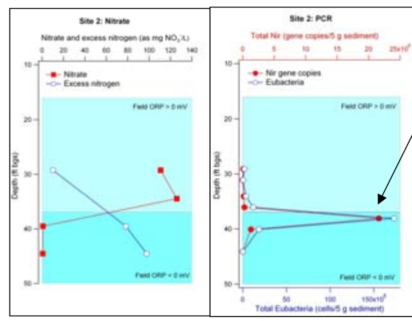
Nitrate and excess N_2 were determined in DP samples within 20 minutes, and used to screen nested monitor wells across a sharp vertical redox gradient

G Bryant Hudson & field-portable MIMS

Excess nitrogen indicates saturated-zone denitrification at **or** upgradient of the sampling point.

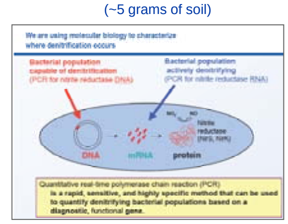
Excess nitrogen allows one to reconstruct
- initial nitrate in recharge water, and
- the extent of denitrification

Using a molecular method to localize the zone of denitrification



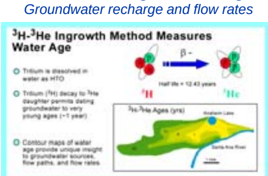
Bacterial population profiles show that denitrification occurs at the oxic-anoxic interface

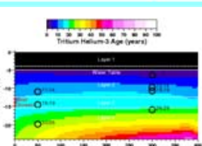
PCR for nitrite reductase (~5 grams of soil)



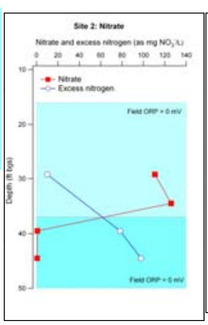
Using groundwater age dating to constrain denitrification rate
(>2.5 g NO_3^-/year/cubic meter sediment at the Kings County site)

Tritium/Helium-3 groundwater age
Groundwater recharge and flow rates

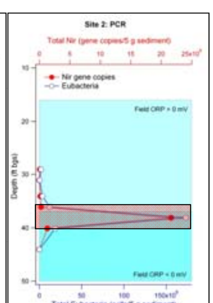




Excess nitrogen
Mass nitrate denitrified

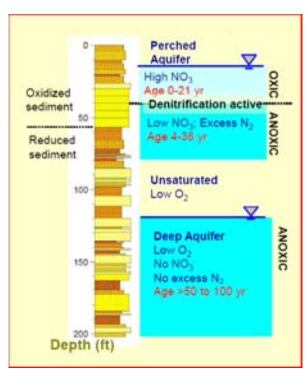


Nitrite reductase PCR
Denitrification zone



Carle, S. F., Moran, J. E., and Esser, B. K., 2010. Denitrification at a Dairy Site Supported by Gas-Liquid Phase Modeling of ³H-³He Groundwater Age. *Toward Sustainable Groundwater in Agriculture - An International Conference Linking Science and Policy (June 15-17, 2010; San Francisco).*

Distinguishing different mechanisms for the occurrence of low-nitrate groundwater in two aquifers underlying the same dairy farm

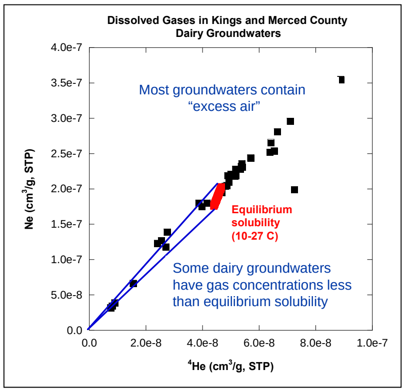


Methods
- Groundwater tritium/helium-3 age dating
- "Excess" and initial nitrogen by MIMS
- Nitrite reductase PCR

Upper aquifer protected by denitrification
- **Dairy operative** during groundwater recharge
- **High nitrate** in recharge waters
- **Denitrification** has occurred and is active

Lower aquifer protected by transport
- **Pre-dairy recharge** of groundwater
- **Low nitrate** in recharge water

Dairy groundwaters show evidence for gas loss



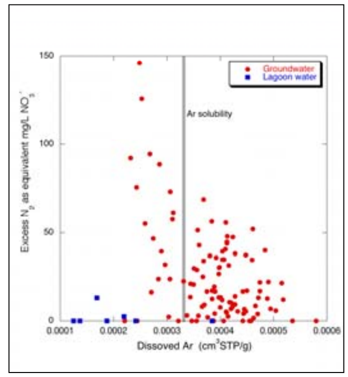
Gas loss is important to identify and quantify

- Affects calculation of **"excess" nitrogen** (and of initial nitrate and extent of denitrification)
- Affects calculation of **^{3}He from tritium decay** (and groundwater age)

Two mechanisms may be responsible

- Gas stripping by CO_2 and CH_4 generated **by biogenic activity in manure lagoons**
- Gas stripping by nitrogen generated by **denitrification**

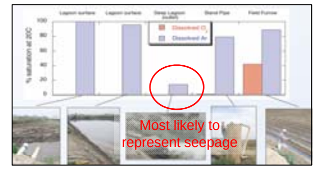
Gas loss in dairy groundwater is often correlated with excess nitrogen and denitrification



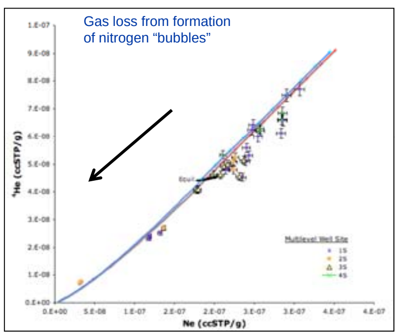
We have observed that gas-stripped dairy groundwaters are often denitrified at this and other dairies

- We see this pattern in wells monitoring fields not affected by lagoon seepage

We also see gas-stripping in in manure lagoon waters and in wells monitoring lagoon seepage



A simple model for gas loss driven by denitrification is consistent with gas data at our Kings County dairy site



Denitrification degassing model (Visser, 2007)

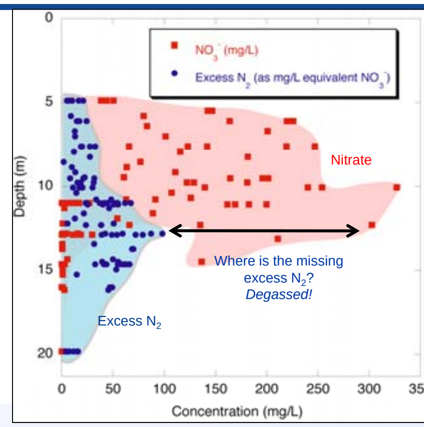
- Excess nitrogen from denitrification
- Dissolved nitrogen exceeds solubility
- Other gases partition into nitrogen bubbles under solubility control

Denitrification is a primary mechanism for gas-stripped groundwaters at dairy sites

Brennwald, M. S., Kipfer, R., and Imboden, D. M., 2005. Release of gas bubbles from lake sediment traced by noble gas isotopes in the sediment pore water. *Earth and Planetary Science Letters 235, 31.*

Visser, A., Broers, H. P., and Bierkens, M. F. P., 2007. Dating degassed groundwater with 3H/3He *Water Resources Research 42, W10434 (1-14).*

Gas loss driven by denitrification can lead to underestimation of excess nitrogen and extent of denitrification



Gas loss does explain the discrepancy between nitrate in the upper oxic aquifer and excess nitrogen in the lower anoxic aquifer

Gas loss can also affect tritium/helium-3 groundwater ages

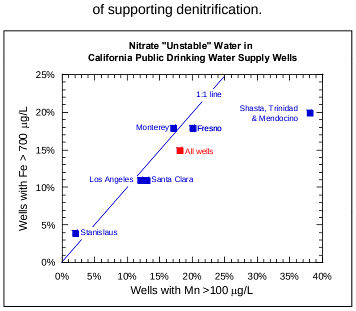
- Ages are underestimated if gas loss is not recognized (~2-4 years at this site)

Dissolved gas analysis of dairy groundwater is a powerful tool for constraining denitrification and gas loss in dairy groundwaters

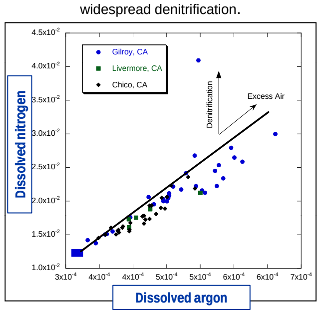
How common is denitrification in California groundwaters?

Proxies for denitrifying conditions and studies using "excess" nitrogen indicate that denitrification does occur in shallow groundwater, but is not common

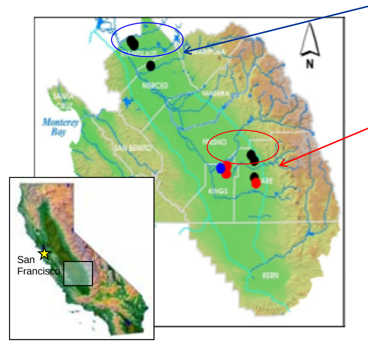
About 15% of public drinking water supply wells in California produce high-Fe, Mn water capable of supporting denitrification.



Groundwater studies in two coastal and one Central Valley basin found no evidence for widespread denitrification.



We participated in a large study of nitrate in first-encounter groundwaters under dairies in the San Joaquin Valley of California



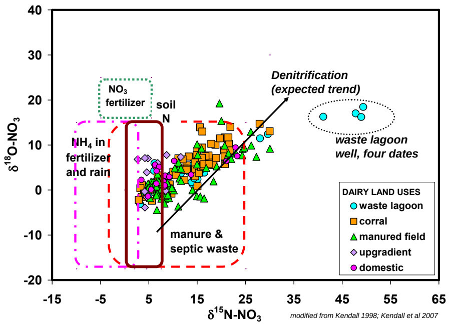
Lower San Joaquin Valley Basin
(Stanislaus & Merced Counties)
Higher groundwater vulnerability: shallow groundwater table, sandy soils, discharges to surface waters

Tulare Basin
(Kings & Tulare Counties)
Lower groundwater vulnerability: deeper groundwater table, heterogeneous sediments; no discharges to surface waters.

Funding: State of California

- Thomas Harter (UC, Davis): Installation of new monitor well network; sampling of groundwater & sediment samples
- Carol Kendall and Megan Young (USGS): Nitrate isotopic composition analyses of underlying groundwaters
- Sustainable Conservation: Funding for LLNL analyses

USGS data on groundwater nitrate isotopic composition indicates that denitrification does occur, but is not ubiquitous



Groundwater nitrate isotopic composition was determined by Megan Young (USGS)

The most enriched samples also have low dissolved oxygen and nitrate. For other samples no relationship exists between isotopic enrichment and NO_3 or DO concentration.

There is evidence of natural nitrate attenuation from denitrification in a few of the wells, but significant denitrification does not appear to be occurring in many of the wells. Young et al (2000)

Young, Harter, Kendall, and Silva (2009). Application of nitrate and water isotopes to assess of groundwater quality beneath dairy farms in California AGU2009 Fall Meeting H31C-0797

Evidence for and against denitrification in dairy groundwaters

Evidence supporting saturated-zone denitrification

- Enrichments in nitrate-^{15}N and –^{18}O
- Characteristic slope on dual-isotope plot
- Low NO_3^- and DO for the most isotopically enriched samples
- Reducing conditions in dairy groundwaters
- Demonstrated denitrification in dairies in area

Evidence not supporting saturated-zone denitrification

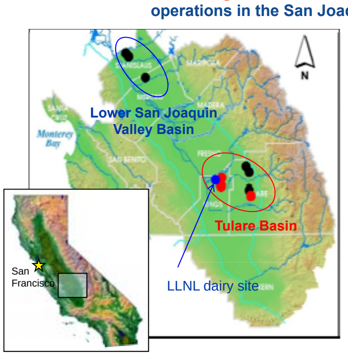
- Isotopic enrichment not correlated with low nitrate for most samples
- Many groundwaters are oxic and have high nitrate
- Alternative hypothesis: **Nitrate isotopics in dairy groundwater record source, not a saturated-zone process**

Is saturated-zone denitrification occurring? → **Measure "excess" nitrogen in groundwater samples**

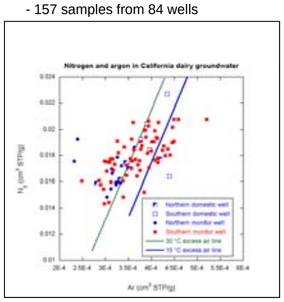
Does dissolved nitrate isotopic composition record source and not denitrification? → **Measure nitrate isotopic composition in vadose-zone sediment samples**

Dissolved gases in dairy groundwaters:
Is denitrification occurring in the vadose zone?

We measured dissolved gases in first-encounter groundwaters underlying dairy operations in the San Joaquin Valley of California



Dissolved gas samples: 9 dairy farms
- 157 samples from 84 wells

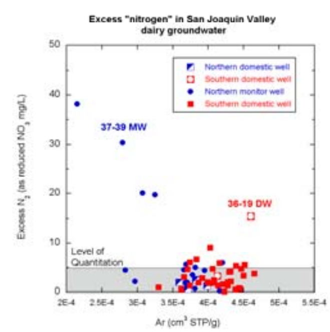


Dissolved gas data shows that denitrification does occur,
but is not ubiquitous and in most cases not protective

Saturated-zone denitrification observed but uncommon

- "Excess" nitrogen seen in groundwaters with the most enriched isotopic compositions
- Significant denitrification accompanied by gas loss seen in shallow northern dairy wells monitoring lagoons and corrals.
- Significant denitrification without gas loss seen in deeper domestic wells

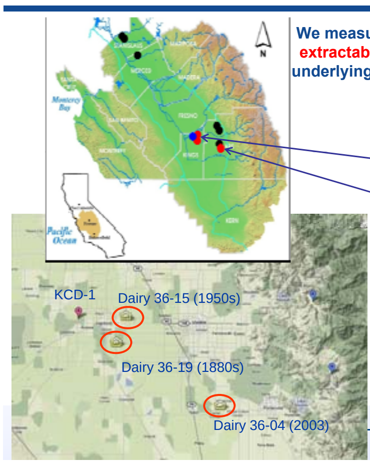
Emphasis on first-encounter groundwaters may miss denitrification occurring deeper within the aquifer



Soil leachate nitrate isotopic composition:
Is the groundwater "denitrification trend" as source signal?

We measured the isotopic composition of water-extractable nitrate from vadose-zone sediments underlying three dairies in the San Joaquin Valley

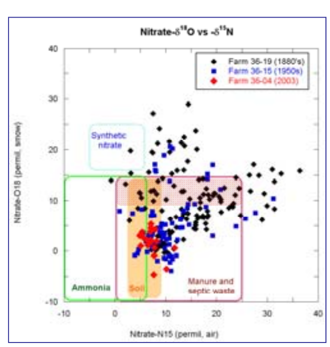
Vadose-zone: 25-40 m (85-140 ft)
- 220 samples from 15 cores

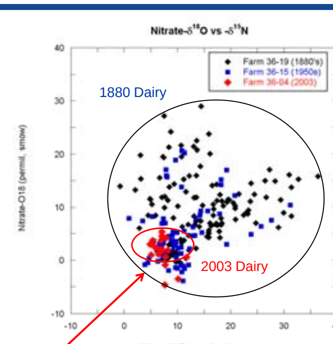


Funding: State of California

- **Thomas Harter (UC, Davis):** Installation of new monitor well network that provided sediment samples
- **Sustainable Conservation:** Funding for LLNL analyses: groundwater dating & dissolved gas; soil nitrate isotopic composition
- **Carol Kendall and Megan Young (USGS):** Nitrate isotopic composition analyses of underlying groundwaters

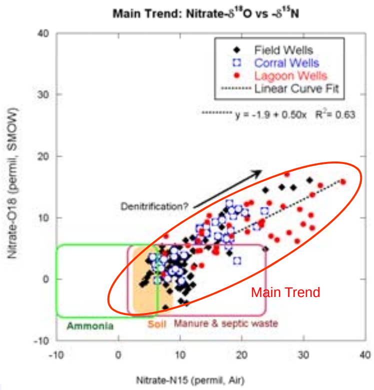
The sediment nitrate compositions and the evolution of this signal over time are consistent with a dairy manure source





Similar isotopic composition observed in domestic wells in the same basin un-impacted by agriculture

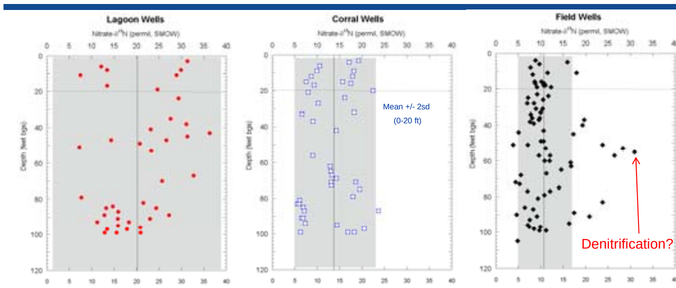
Sediments with >1mg/g of leachable nitrate that fall on an isotopic trend line with a slope characteristic of denitrification



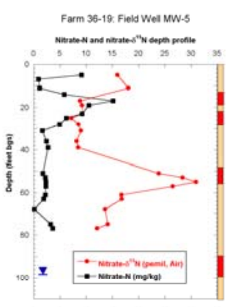
Main trend sediments fall along a correlation line that is consistent with denitrification (slope = 1/2)

- Nitrate-δ^{15}N vs nitrate-N patterns are not simple, and vary with overlying land use
- **This pattern in the vadose-zone indicates that the same pattern in first-encounter groundwaters may not indicate saturated-zone denitrification**

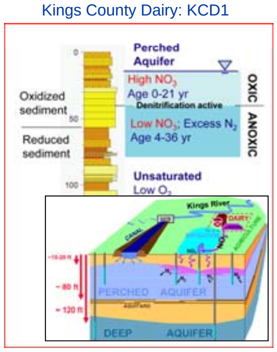
Nitrate-δ^{15}N depth profiles show preservation of source signal during transport through vadose zone for lagoon & corral wells; and localized denitrification in individual field wells



In one field core, denitrification occurs at a similar depth as in the saturated zone under a nearby dairy in the same basin

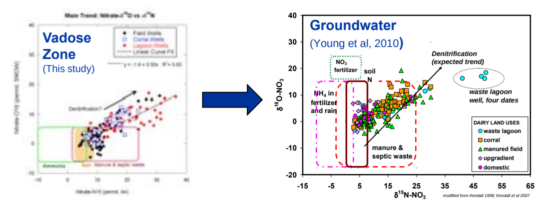


Kings County Dairy: KCD1



Denitrification does occur in the saturated zone, and may occur in the vadose zone underlying large dairy operations.

Nitrate isotopic composition in oxic, high-nitrate groundwaters underlying dairies records source, not saturated-zone denitrification



- Dairy vadose-zone nitrate is variable in isotopic composition, but consistent with a manure source
- Dairy vadose-zone nitrate is similar to saturated-zone nitrate, but also include high- δ^{18}O samples
- Nitrate is transported through the vadose zone without significant isotopic fractionation
- Most moderate to high-nitrate vadose-zone sediments fall on a "denitrification" trend

The "denitrification trend" in dairy groundwater is likely a source signal and does not indicate wide-spread saturated zone denitrification

Policy implications

- **Denitrification is an important process to consider in assessing the impact of large dairy operations on groundwater quality**
  - Denitrification mitigates the impact of nutrient loading
  - Denitrification may be an important term in nutrient budget models of groundwater nitrate on the local and regional scale
  - Denitrification affects nitrate isotopic composition and source attribution
  - Denitrification may be accompanied by gas loss, which can affect groundwater age dating and the calculation of excess nitrogen
- **Information necessary to evaluate denitrification should be collected when monitoring impacted groundwaters**
  - *Groundwater redox:* ORP, DO, Fe, Mn, NO3-
  - "***Excess" nitrogen:*** **MIMS or GCMS analysis of N_2 and Ar**
  - *Nitrate-N and nitrate-O isotopic composition*
- **In addition to first-encounter site wells, deeper domestic and monitor wells should be tested for denitrification and denitrifying conditions**

Technical conclusions

- **Determination of excess nitrogen in groundwater requires that atmospheric gas content be measured, not assumed**
- **Gas loss does occur in dairy groundwater, and can affect calculation of excess air and of tritium/helium-3 groundwater age**
- **Vadose-zone nitrate isotopic composition in sediments underlying dairies indicate that the "denitrification" trend in first-encounter groundwaters is a source signal and does not result from saturated-zone denitrification**

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